Effects of Temperature on Activation Energy and Pre-Exponential Factor in C-C Bond Forming Reactions Using a Cooperative Aminosilica Catalyst

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In the organic synthesis of chemical products, the formation of covalent carbon-carbon bonds is consistently an essential process in the production of important molecules. Overcoming the activation energy of these various reactions often requires a catalyst consisting of a transition metal. These metals are expensive and can deactivate and/or deteriorate over time. Silica based catalysts are easily synthesized, and do not require the rare elements needed for some metal-based catalysts. These silica materials contain surface silanols that can act as weak acids in chemical reactions. These silanols react with trialkoxysilanes bearing functional groups such as amines and carboxylic acids to impart different catalytic effects. Incorporating basic amines on these silica surfaces allows for cooperative catalytic behavior, in which the material has acidic and basic properties that can participate in the catalytic process without deactivating each other. In addition to their catalytic nature for organic synthesis, amine-functionalized silicas also have promising results in CO_2 capture, making them an interesting topic for study. In this study, effects of temperature in aldol and nitro-aldol condensations facilitated by amine-loaded, silica based catalysts is observed.

In this study, we chose 4-nitrobenzaldehyde as the substrate because the strong electron-withdrawing group in the para position increased the catalytic activity for each reaction. The aldol and nitro-aldol condensations use acetone and nitromethane, respectively, as solvents and reactants. The active catalyst is an MCM-41 silica catalyst with (4-aminobutyl)triethoxysilane grafted on the surface. Physical and chemical characterization of the catalyst is confirmed using physisorption, XRD, and TGA. A HDMS capped version of the catalyst is used as a control to ensure that cooperative catalytic activity is, in fact, from the grafted amine groups and silanols. We performed the aldol and nitroaldol condensations on the aminosilica catalysts at four different temperatures to determine the initial activity at each temperature. The kinetic results for each trial allow for the activation energy and pre-exponential factor to be calculated for the two reactions. Our results indicated that the aldol condensation has a higher activation energy than the nitro-aldol, and that both activation energies are lowered when the silanols are uncapped. These results suggest that silica based catalysts, upon further research, could have a large impact on the chemical industry involving organic synthesis.